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Lincoln, Jason, E
Curliss, David, B
Brown, Thomas, J, Jr.

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Performance Polymer Solutions, Inc.
2711 Lance Dr.
Moraine, OH 45409

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Dr. Jocelyn Harrison
Air Force Office of Scientific Research
875 North Randolph Street, Room 3112
Arlington, VA 22203-1995

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Report developed under STTR contract for topic number AF10-BT01. The recent Small Business Technology Transition (STTR) program was focused on the thermal property enhancement of polymeric composites using various functionalizations and treatments of pitch carbon fiber surfaces. The pitch based carbon fibers were first reacted with a maleic anhydride solution to increase the functionality of the fiber surface. The reactive surface was then treated with four various primary amine structures that would provide a surface coupling to the polymeric matrix. The surface chemistry was evaluated at each stage by X-ray Photoelectron Spectroscopy (XPS). Both two-dimensional and three-dimensional fiber constructions were evaluated with epoxy and polyimide based matrix resins. All results and findings are included in this Final Technical Report.

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**Contractor Information:**

Jason E. Lincoln, PhD
Performance Polymer Solutions Inc. (P$^2$SI)
2711 Lance Drive
Moraine, OH 45409
Tel: (937) 298-3713
Fax: (937) 298-6615
E-mail: jason.lincoln@p2si.com

**Delivered to:**

Dr. Joycelyn Harrison
AFOSR/RSA
875 North Randolph Street
Suite 325, Room 3112
Arlington, VA 22203
Phone: 703.696.6225
joycelyn.harrison@afosr.af.mil

Roger Gerzeski
Roger.gerzeski@wpafb.af.mil

technicalreports@afosr.af.mil

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# GLOSSARY

| Variable/Acronym | Description | Typical Units |
|---|---|---|
| 2D | Two-Dimensional | - |
| 3D | Three-Dimensional | - |
| MSU | Michigan State University | - |
| NMP | N-methyl-2-perolidone | - |
| P$^2$SI | Performance Polymer Solutions Inc. | - |
| PAN | Polyacrylonitrile | - |
| ppi | picks per inch | picks/in |
| RFPE-CVD | Radio frequency plasma enhanced – chemical vapor deposition | - |
| SEM | Scanning electron microscopy | - |
| STTR | Small Business Technology Transition | - |
| TFAH | Trifluoroacetylacetone | - |
| UVO | Ultraviolet light/ozone | - |
| XPS | X-ray Photoelectron Spectroscopy | - |

# 1. SUMMARY

The recent Small Business Technology Transition (STTR) program was focused on the thermal property enhancement of polymeric composites using various functionalizations and treatments of pitch carbon fiber surfaces.  The pitch based carbon fibers were first reacted with a maleic anhydride solution to increase the functionality of the fiber surface.  The reactive surface was then treated with four various primary amine structures that would provide a surface coupling to the polymeric matrix.  The surface chemistry was evaluated at each stage by X-ray Photoelectron Spectroscopy (XPS).

Several pitch fiber reinforced polymer matrix composites were fabricated and evaluated by thermal conductivity and flexure strength.  Three-dimensional pitch fiber preforms were utilized in the composite structures to provide a through-thickness pathway for thermal transport.  High temperature matrix resins were evaluated for the potential for high temperature, high thermal conductivity pitch fiber composites to enable higher temperature structures with more efficient heat transfer.  All results and findings are included in this Final Technical Report.

# 2. INTRODUCTION

This Small Business Technology Transition (STTR) Program was designed to develop and demonstrate a thermally conductive structural graphite fiber reinforced hybrid matrix composite material with a through-thickness thermal conductivity of up to 20 W/m·K. This novel structural prepreg material will be developed through engineering of an optimal fiber/matrix interphase conducive to phonon transport, in combination with P$^2$SI's high temperature matrix resins for continuous pitch fiber composites. The new engineered interphase, formed in a continuous production process, will be directly applicable to a broad range of continuous pitch fibers, including those of novel surface morphologies, such as P$^2$SI's carbon nanotube fused fibers and pitch fibers containing graphene nanofin morphologies.

In the Phase I effort, the engineered interphase is being developed through modifications to the fiber surface using Michigan State University's ultraviolet-ozone (UVO) coupling technique in combination with P$^2$SI's carbon fiber surface chemistry already demonstrated on polyacrylonitrile (PAN) carbon fibers. Specifically, the carbon fiber surface will be linked to the polymer matrix by covalently bonded molecules engineered to minimize interfacial contact resistance between the matrix bulk and the fiber surface. By combining our UVO treatment with the new chemical modifications developed here, and recently developed hybrid matrix, the program objective for composite through-thickness thermal conductivity will be achieved.

The formation of graphene nanofins on the surface of the pitch carbon fibers was also explored for the enhancement of transverse thermal conductivity of the fiber itself. Typically, the as-received pitch fibers have tremendous axial thermal conductivity; however, the transverse thermal properties are limited by the orientation of the graphene planes within the fiber. The formation of graphene fins oriented normal to the fiber direction should provide pathways for phonon transport transverse to the fiber direction, and therefore through the thickness of the composite.

In any respect, the graphene sheets will share the deficiencies of the parent fiber with regard to surface functionality and the ability to bond to aerospace resin systems. They should, however, respond equivalently to the surface modifications being proposed in this work. Therefore, in this STTR program, we have investigated the potential for this unique graphene fin morphology to benefit overall composite thermal conductivity.

# 3. METHODS, ASSUMPTIONS, AND PROCEDURES

## 3.1 Graphite Fiber Surface Chemistry Modifications

### 3.1.1 Maleic Anhydride Treatment

P[2]SI previously demonstrated a novel approach to engineer the surface functionality of carbon fibers by reacting maleic anhydride (MA) with graphitic edge planes on the fiber surface, as shown schematically in Figure 1.  This anhydride surface functionality can be reacted with a variety of groups compatible to epoxy and bismaleimide resins.  Both difunctional and asymmetric molecules can then be used to link the resin to the fiber surface through rigid or flexible covalent bonds, enabling a broad design space for interface engineering.
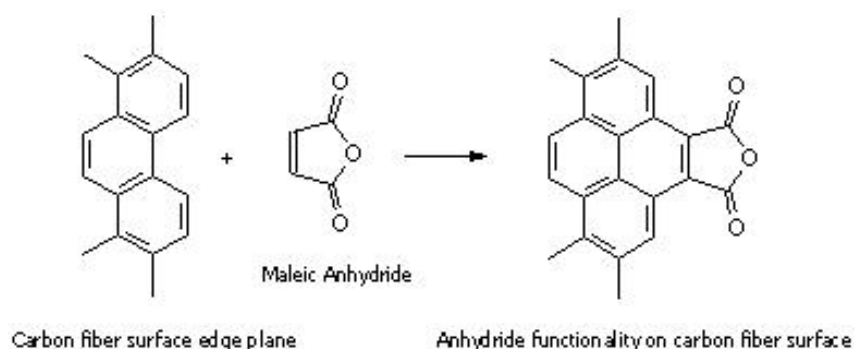


Maleic Anhydride

Carbon fiber surface edge plane          Anhydride functionality on carbon fiber surface

**Figure 1. Graphite Surface Modification by Maleic Anhydride Edge Plane Reaction**

To perform the maleic anhydride surface treatments, a short length of CN80-30s pitch carbon fiber, supplied by Nippon Graphite Fiber Corporation, was cut, de-sized in acetone, and dried at 100°C for several minutes.  The fiber was wrapped around a short, one inch diameter quartz tube, approximately 2 inches long and held in place using Teflon® tape on the edges of the tube.  The quartz tube was then placed into a 1000 mL cylindrical glass reactor with a 1% solution of maleic anhydride in toluene.  The solution was then set to boil for approximately two hours at 145°C.
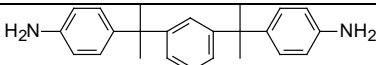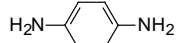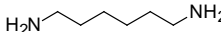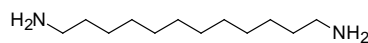
Following the two hour maleic anhydride boil, the reactor was cooled to below 75°C and the fiber spool was removed.  The fiber was washed with hexanes to remove the toluene and dried at 100°C over night.  The treated fiber was then shipped to Michigan State University (MSU) for chemical surface analysis by X-ray Photoelectron Spectroscopy (XPS).

### 3.1.2 Diamine Functionalization

Once the fiber surfaces were functionalized with maleic anhydride, the fibers were then reacted with various diamines to provide a covalently bonded link between reinforcing fiber and polymer resin matrix.  The diamines chosen for the initial study are shown in Table 1.  To apply the amine functional groups to the anhydride modified surfaces, each diamine was dissolved to form a 1 wt % solution in an 80/20 mixture of tetrahydrofuran/methanol.  The strands of anhydride

functionalized fiber were then placed into the solutions, one per 1000 mL beaker. The fibers were left in solution over night, then removed and rinsed with methanol, dried, and sent to MSU for XPS surface analysis.

**Table 1. Diamine Coupling Agents Used for Surface Modifications**

| Coupling Molecule | Structure |
|---|---|
| Bisaniline-M | $H_2N$—⟨benzene⟩—⟨benzene⟩—⟨benzene⟩—$NH_2$ |
| *p*-Phenylenediamine | $H_2N$—⟨benzene⟩—$NH_2$ |
| Hexamethylenediamine | $H_2N$⌒⌒⌒$NH_2$ |
| Dodecamethylenediamine | $H_2N$⌒⌒⌒⌒⌒⌒$NH_2$ |

Analyzing the XPS data from the initial diamine functionalization, it was apparent that the surface chemistry of the fiber was successfully altered. However, it was unknown how much of an effect the maleic anhydride treatment had on the diamine functionalization. To determine the efficacy of the maleic anhydride treatment, several lengths of desized pitch carbon fibers were functionalized with diamines, without prior maleic anhydride treatment. Four 1% diamine solutions in an 80/20 mixture of tetrahydrofuran/methanol were formulated, one for each diamine listed in Table 1. 200 cm lengths of desized CN80 pitch carbon fiber were then placed into the solutions, and left over-night. The following morning, the fibers were removed from the diamine solutions, rinsed with methanol, and placed in a 100°C oven to dry for several hours. After the samples were sufficiently dry, the fibers were removed from the oven, placed into individual bags, and sent to MSU for XPS analysis.

Simultaneous to the previous diamine functionalization of desized pitch carbon fiber, UVO treated fiber was also investigated for diamine functionalization. The UVO treatment of pitch carbon fiber is an alternate mode of oxidizing the surface of the fiber to provide a more reactive surface for further chemical manipulation. The UVO process enables low temperature, rapid, pollutant-free oxygenation of the pitch carbon fiber surfaces which, in turn dramatically enhances wetting (van der Waals interaction) and covalent bonding adhesion of the polymer matrix system to the pitch carbon fibers. The treatment was performed by MSU on their continuous UVO production line. The oxidized fibers were further functionalized with the four diamine solutions, as described above.

With successful diamine functionalization of the pitch fiber surface, work was moved towards fabricating functionalized pitch fiber composites. A continuous diamine treatment line was designed and constructed, consisting of a large dip bath and drying furnace with an automated re-spooler. The desized pitch fiber was affixed to the treatment line, passing through the diamine treatment bath and drying furnace before being wrapped onto a core and used for unidirectional tape fabrication. Figure 2 shows the continuous diamine treatment dip bath.

**Figure 2. Continuous Diamine Treatment Dip Bath**

Following analysis of the functionalized composites, it was determined that the dodecamethylenediamine surface treatment provided the greatest enhancement in both thermal and mechanical properties. Therefore, dodecamethylenediamine was utilized for the remaining work.

### 3.1.3 X-Ray Photoelectron Spectroscopy

Following fiber surface treatments, each yarn was packaged and sent to Michigan State University for X-Ray Photoelectron Spectroscopy (XPS) surface analysis. XPS is a quantitative spectroscopic technique that measures the elemental composition and chemical state of a material's surface. To obtain spectra, the material surface is irradiated with a beam of X-rays while simultaneously measuring the number of, and kinetic energy of escaped electrons. The kinetic energy is then correlated to the binding energy of the electron, indicating the chemical bond it was associated with, as each bond has a relatively unique binding energy. The number of electrons detected is also related to the comparative concentration of the bond, representing overall chemical construction and morphology of the material. In this instance, the XPS analysis was a technique used to measure the effectiveness of the various surface treatments.

XPS measurements were performed using a Physical Electronics PHI-5400 ESCA work station. X-ray photons were generated from a polychromatic Mg anode (1254 eV). The analyzer was operated in the fixed energy mode employing a pass energy of 89.45 eV for survey scans and 17.9 eV for utility scans.

## 3.2 Pitch Fiber Nanofin Modifications

In an effort to enhance the transverse thermal conductivity of the fiber itself, nanofin modifications were attempted by Radio Frequency Plasma Enhanced Chemical Vapor Deposition (RFPE-CVD). It has been reported in literature [1, 9] that the formation of graphene nanosheets, oriented normal to the fiber direction is possible with a plasma enhanced chemical vapor deposition process. In the reports, uniformly spaced nanosheets were systematically grown from the surface of pitch based carbon fibers, without the use of a catalyst. The graphite surface itself provides a nucleation site for the monolithic growth of these nanostructured graphite sheets. The graphene fin morphology then offers a potential increase in the thermal conductivity normal to the fiber axis, which can favorably impact composite through-thickness thermal conductivity.

The nanofin processing methods provided in literature, however, utilize a microwave plasma technique, not conducive to continuous manufacturing. Therefore, in the current work, a RFPE-CVD technique was explored for the formation of graphene sheets.

To test the applicability of the RFPE-CVD process, a small testing matrix was developed with various processing conditions for the growth of nanofins on the surface of pitch carbon fibers. The fibers were first oxygenized by an ultraviolet light/ozone (UVO) surface treatment. In this case, the oxygenation provides a nucleation point for growth of graphene nanofins, extending from the edge planes of the fiber itself. Following UVO treatment, the fibers were then subjected to the RFPE-CVD conditions summarized in Table 2. For each case, the plasma power would was held at 600 W, pressure at 30 Torr, frequency at 13.56 MHz, 10 sccm methane flow rate, and 50 sccm hydrogen flow rate. Each testing condition was evaluated by scanning electron microscopy (SEM).

**Table 2. Testing Matrix for Nanofin Formation**

| Condition Number | Temperature (°C) | Growth Time (min) |
|:---:|:---:|:---:|
| 1 | 750 | 10 |
| 2 | 750 | 20 |
| 3 | 800 | 5 |
| 4 | 800 | 10 |
| 5 | 800 | 20 |

### 3.2.1 Michigan State University Nanofin Modification Work

Michigan State University investigated the use of radio frequency plasma to grow petal-like carbon nanofin outgrowths on carbon fibers per the methodologies reported by Bhuvana *et al*. [1], which used microwave plasma chemical vapor deposition. The MSU unit is a "cold" plasma using RF excitation to strike the plasma. Furthermore, the MSU unit is of lower power, limited to 550W peak output, significantly lower than the microwave plasma of 900W reported in [1]. The MSU unit was installed and experiments were conducted on a series of carbon fibers in the RF plasma chamber.

The use of microwave plasma chambers owned by others at MSU was also explored as a means to grow carbon petal-like structures on carbon fibers.  Although MSU has experience in microwave plasma treatment of carbon fibers, significant barriers now exist in accessing these units for this present work.  A literature review shows that the use of cold plasmas can be used to grow carbon structures on fibers, however, the fibers must be heated to 1000 K or more during the treatment.   The literature confirms our previous unsuccessful efforts at growing carbon nanostructures using the cold plasma chamber, which does not have the capability of heating the specimen.  These high temperatures are also known to damage the tensile strengths of the pitch fibers, therefore we focused our work on RF growth.

### 3.2.1.1 Plasma Treatment of Fibers

A series of carbon fibers (pitch and PAN based) were used to provide a range of substrates to initiate the growth of the petal-like outgrowths. A pitch fiber, Granoc CN80, that had been thermally desized was supplied by $P^2SI$, a PAN derived fiber (AS4-12k) and another pitch fiber (Dialead K63712) that had not been sized were also treated.

A section of tow was crimped with foil at each end to prevent the fibers from floating free in the treatment chamber.  The ends of the tow were placed on ¼" thick glass bars and weighed down with another glass bar. The pitch fiber tows were rigid enough to span the distance between the bars without touching the support shelf, the AS4 required some applied tension to keep it from resting on the shelf. The fibers were first cleaned in a pure $O_2$ plasma for 30 minutes. The $O_2$ flow rate was 500 sccm and the power was 75% of full scale (412 W).  The growth phase gases were $CH_4$ and $O_2$ in a 20:1 ratio (200 sccm & 10 sccm), as used in the paper. The tows were treated for 60 minutes at 75% power.  At steady state, the operating pressure of the chamber was ~0.130 Torr and the temperature was 30°C. The fibers were examined using the Zeiss EVO SEM.

A second treatment was conducted at low power, 1% of full scale, to determine if the growth of the structures would be favored in a less energetic plasma.  The gas flow rates and treatment time were the same as before.

### 3.2.1.2 Previous Carbon Fiber Treatment Work

In the mid-1990s, there was a substantial thrust at MSU for exploring the use of microwave plasma technology to process composite materials.  This effort was based on the collaborations between composite process engineers and microwave plasma experts in the College of Engineering.  During this period carbon fibers were subjected to chemical vapor deposition using microwave plasma generators. By varying the composition of the gases and the microwave power, various carbonaceous structures were grown on the fibers.  Figure 3 shows unpublished work from these exploratory efforts detailing the formation of four distinct morphologies that were grown on carbon fibers.
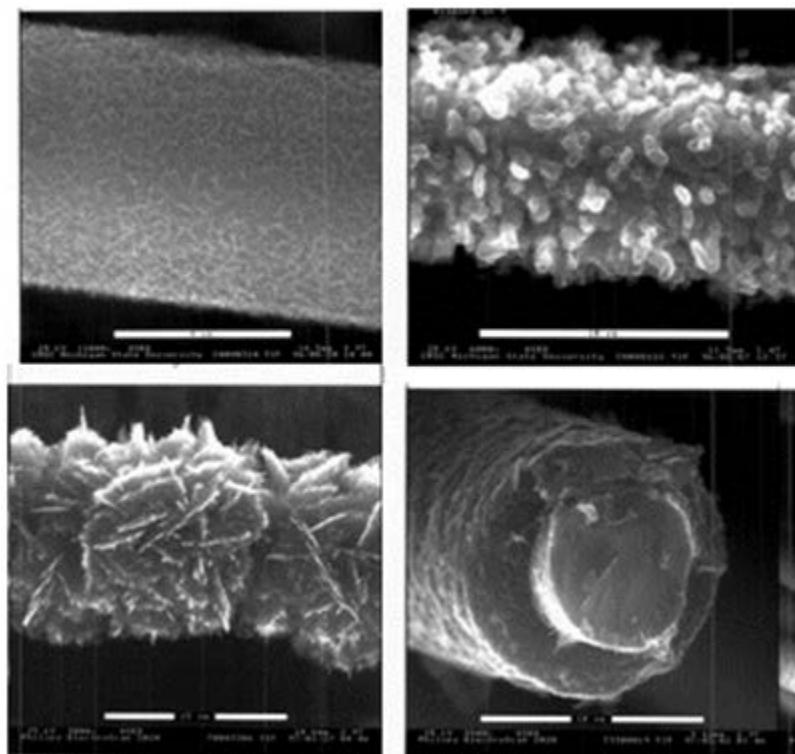
**Figure 3. Micrographs of Carbon Nanostructures Grown on Carbon Fibers Using Microwave Generated Plasmas at MSU**

### 3.3 Silver Polyimide Formulation

In addition to the fiber surface modification work, an alternate resin formulation was also investigated for improving the overall composite transverse thermal conductivity by providing a thermally conductive matrix. It has been reported in literature [12-14] that thermally conductive polyimide films are feasible with incorporation of a silver(I) complexs into a poly(amic acid) resin solutions. Thermal cure of the resin system leads to cycloimidization with the silver(I) reduction, yielding a reflective and conductive silver surface. Integrating this technology into pitch fiber composites may further enhance the transverse thermal properties of the composite and provide higher temperature thermally conductive composite materials than achievable with traditional epoxy or bismaleimide matrices.

The initial attempt at fabricating a metalized polyimide resin system involved the addition of a silver(I) $\beta$-diketone complex to a previously prepared 30% poly(amic acid) resin solution. A silver(I) acetate powder was first slurried with a 1.35 equivalent of triflouroacetylacetone (TFAH) in N-mehtyl-2-pyrrolidone (NMP). The poly(amic acid) was then added to the slurry, creating a gelled, homogenous doped resin. In this work, a silver concentration of 13% was used for the metalized polyimide.

Following silverized resin fabrication, a layer of the doped resin was spread across the surface of a 2 inch by 2 inch T650-35 PAN carbon fabric sample and thermally cured to investigate the

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applicability of the resin in composite manufacture. The metalized lamina was analyzed for thermal conductivity, although the single ply was not flat and parallel on the faces, leading to unreliable results.

## 3.4 Pitch Fiber Composite Fabrication

### 3.4.1 Epoxy Matrix Composites

The primary focus of this Phase I work was the enhancement of through-thickness thermal conductivity in pitch fiber reinforced epoxy composites. Several measures were taken in achieving this goal, including the use of three-dimensional fabric preforms, amine functionalization, and application of high thermal conductivity nickel coatings.

### 3.4.1.1 Three-Dimensional Pitch Epoxy Composites

Several three-dimensional pitch fiber preforms, 3 mm thick, were purchased from 3Tex Inc. with varying fill insertion densities of 5-9 picks per inch (ppi). These preforms were non-crimp, orthogonal fabrics. The preforms contain pitch fibers in both the warp (YS95) and Z-direction (YS80) with a PAN fiber (AS-4) in the fill direction. 152 by 152 mm sheets were cut from the pitch fiber preforms and vacuum infused with an EPON 862, Epikure W epoxy resin system at 60°C. Once infused, the panels were partially cured at 121°C for 32.5 minutes to reduce processing viscosity. Each part was then loaded into a 152 by 152 mm compression mold and into a Wabash hydraulic press. The parts were then heated under contact pressure to 121°C. A pressure of 0.689 MPa was then applied to the part and held for one hour. The parts were then heated to 177°C and held for an additional hour. Following the hour long hold at 177°C, the part was then cooled while maintaining the 0.689 MPa pressure. Once under 121°C, the pressure was released and the parts were removed from the mold.

The three-dimensional pitch fiber composites were machined for microscopy, thermal conductivity, flexure testing, and short beam shear testing. Microscopy images were taken in both the warp and fill directions of each panel to show the particular fiber orientation. The microscopy samples were 38.1 mm by 12.7 mm. The thermal conductivity samples were 12.7 mm by 12.7 mm. Thermal conductivity testing was performed in-house on a guarded-hot-plate thermal conductivity rig using a modified version of ASTM C177. The modified testing method utilizes a smaller sample size, maximizing material usage. Flexure testing was performed on a table-top Instron 5544 load frame according to ASTM standard D790. The samples were 12.7 mm wide with a length at least 12.7 mm longer than 16 times the specimen thickness. Short beam shear testing was also performed on a table-top Instron 5544 load frame. Testing was performed according to ASTM standard D2344 with samples machined to 6.35 mm width and a length six times the panel thickness. The fiber volume fraction of each panel was also determined using an acid digestion testing method.

### 3.4.1.2 Amine Functionalized Pitch Epoxy Composites

Unidirectional, UVO treated and diamine functionalized pitch fiber composites were fabricated using continuously treated CN80 fibers with dodecamethylenediamine and p-PDA surface

treatments.  The surface treated fibers, as well as a desized CN80 control fiber were drum wound and impregnated with an EPON 862/Epikure W epoxy resin system to form unidirectional prepreg tapes.  Each prepreg was then cut to 6 inch by 6 inch plies and assembled in a unidirectional fashion.  The three laminates were then B-staged (partially cured) for 32 minutes in an air-circulated oven at 121°C, and compression cured at 177°C for one hour.  Following compression cure, the panels were post-cured for an additional hour at 177°C, and then machined for short beam shear, double-notch shear, and thermal conductivity testing.

### 3.4.1.3 Nickel Coated PAN Epoxy Composites

An additional fiber surface treatment in metalized coatings was investigated for composite transverse thermal conductivity improvements.  A nickel coated PAN carbon fiber was in stock at $P^2SI$ and used for this initial study.  The fiber was initially supplied by Technical Fiber Technologies LLC.  The fiber was drum wound and impregnated with an EPON 862/Epikure W epoxy resin system.  The unidirectional prepreg tape was then cut into twelve 6 inch by 6 inch plies and stacked in a unidirectional fashion.  The panel was then B-staged (partially cured) for 32 minutes in an air-circulated oven at 121°C, and compression cured at 177°C for one hour. Following compression cure, the panel was post-cured for an additional hour at 177°C, and then machined for short beam shear, double-notch shear, and in-plane and out-of-plane thermal conductivity testing.

### 3.4.2 Polyimide Matrix Composites

Improved thermal conductance is also a need for high performance composite materials to aide in the spreading of heat away from the organic matrix materials.  Therefore, pitch carbon fiber reinforcements were investigated for use in polyimide matrix composites.  Both unidirectional and three-dimensional pitch fiber composites were considered for this work with a polymerized monomeric reactant (PMR) type polyimide resin matrix.  In addition, a metalized polyimide resin matrix was briefly explored as an increased conductance resin system.

### 3.4.2.1 Unidirectional Pitch Polyimide Composites

Unidirectional pitch fiber, polyimide composites were manufactured in a similar way to the previously discussed epoxy based composite materials.  The pitch carbon fiber (CN80) was first wound onto a laboratory scale drum winder and impregnated with a $P^2SI$ developed polyimide resin.  Once impregnated, the unidirectional tape was removed from the drum and cut into twelve 6 inch by 6 inch plies and assembled in a unidirectional fashion.  Once assembled, the volatiles were driven off and the panels were further imidized and compression cured up to 371°C.

Two unidirectional pitch fiber polyimide composites were fabricated for this work, one with UVO and diamine surface treatment of the pitch fiber and one desized CN80 pitch fiber control for comparison.  Once fabricated, the panels were machined for short beam shear, double-notch shear, and thermal conductivity testing.

### 3.4.2.2 Three Dimensional Pitch Polyimide Composites

Three-dimensional pitch fiber preforms were also investigated for improvement of out-of-plane thermal conductivity in polyimide matrix composites. The 3D polyimide composites were fabricated by initial vacuum infusion of the polyimide resin matrix into the preform with subsequent volatile removal, imidization, and compression cure. The supplied pitch fiber, 3D preforms were first cut to 6 inch by 6 inch dimensions. The preforms were then infused with 55% polyimide resin solution in a small vacuum oven and subjected to imidization and compression cure.

Two 3D polyimide composites were initially fabricated for this work, including one control panel and one desized, ozone treated, and diamine functionalized panel. The cured panels were machined for short beam shear, three-point flexure testing and through thickness thermal conductivity. The resultant panels, however, were porous and not well compacted. Therefore, additional 3D polyimide composites were fabricated with an alternate processing procedure to improve on the quality from the original parts.

### 3.4.2.3 Silver Polyimide Composites

With conceptual success of the silverized laminae, work was moved towards fabricating a 4-ply laminate with CN80-60S pitch carbon fiber. A 6 inch unidirectional tape was drum wound dry with the doped resin spread across the tape, yielding an approximate resin content of 35%. Four plies of the unidirectional tape were then cut and assembled with $[0/90]_s$ sequencing. The part was then dried, compression cured, and post cured to diffuse the silver particles to the surface of the panel. Transverse thermal conductivity was performed using the in-house guarded-hot-plate technique described above.

A second silver polyimide composite was attempted after the initial trial blistered during cure. The second panel was processed similarly, but with a caul plate placed on top of the panel to provide some compaction. The panel was later machined and tested for transverse thermal conductivity using the in-house guarded-hot-plate technique.

# 4. RESULTS AND DISCUSSION

## 4.1 Graphite Fiber Surface Chemistry Modifications

### 4.1.1 Maleic Anhydride Treatment

Analyzing the XPS results of the maleic anhydride treatment, a chemical alteration is apparent. Comparing the prominent peaks of the CN-80 control and maleic anhydride treated fibers, shown in Figure 4, the carbon 1s concentration shifted from 96.35% of the desized CN-80 sample to 93.71% of the maleic anhydride treated sample, and the oxygen 1s concentration shifted from 3.65% of the desized CN-80 sample to 5.35% of the maleic anhydride treated sample. The chemical shift was not significant, but indicated successful functionalization of the fiber surface. The maleic anhydride functionalized fiber could then be further functionalized with the primary amine structures to provide a covalently bonded linkage between the fiber and matrix material.
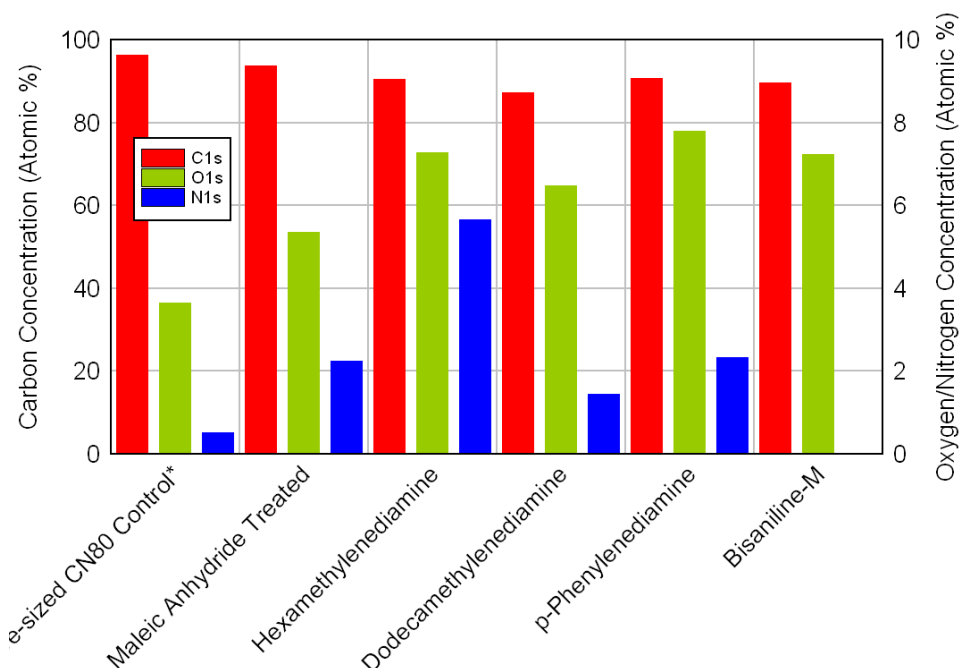


**Figure 4. XPS Surface Chemistry Analysis Results**

### 4.1.2 Diamine Functionalization

The initial diamine functionalization technique proved successful with analysis of the fiber treatment XPS results. The results, shown in Figure 4, indicate a significant increase in nitrogen content between the maleic anhydride treated fiber surfaces and the diamine functionalized fiber surfaces, from 0.52% to a maximum of 5.66%. In addition, the carbon content from the maleic anhydride treated fiber to the diamine functionalized fiber indicates a slight decrease, from 93.71% to a minimum of 87.25%. The change in molecular composition indicates a chemical reaction where one of the primary amines attaches itself to the fiber surface, leaving the second amine to bond with the epoxy resin matrix.

The diamine functionalization of pitch fiber yarn without prior maleic anhydride treatment was also conducted and analyzed by XPS. The results are shown in Figure 5, indicating the primary elemental compounds detected and their relative atomic concentration. When compared to the desized CN80 control, shown in Figure 5, the treatments indicate a reduction in carbon content and an increase in both oxygen and nitrogen content. The results are also comparable to the diamine functionalization results with prior maleic anhydride treatment, demonstrating successful fiber functionalization without maleic anhydride pre-treatment.
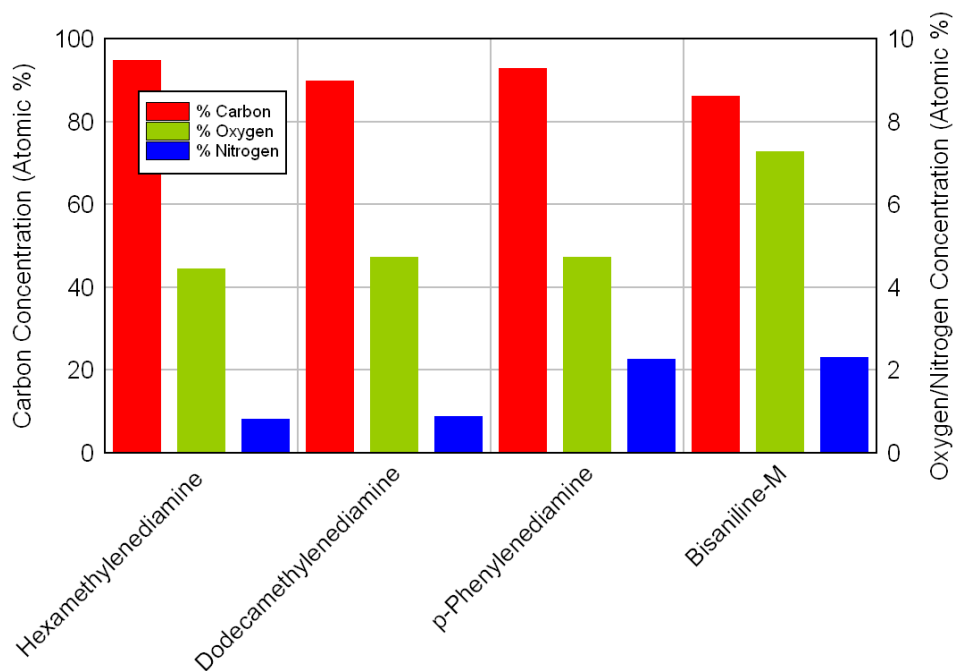


**Figure 5. Diamine Functionalization XPS Results without Prior Maleic Anhydride Treatment**

Fiber functionalization with diamine coupling agents was also explored for UVO treated pitch carbon fiber. The XPS results are shown in Figure 6. The atomic composition of the fibers following diamine functionalization showed little and inconsistent change when compared to the control UVO treated pitch carbon fiber.
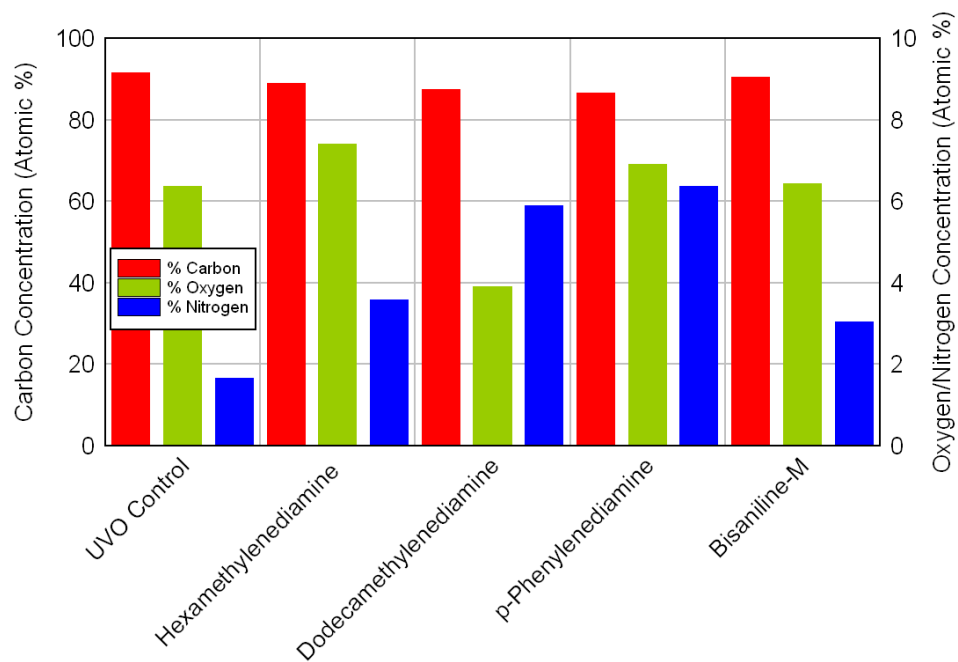
13

**Figure 6. Diamine Functionalization XPS Results of UVO Treated Pitch Carbon Fiber**

The continuous diamine treatment line was successfully assembled. Several one hundred gram spools were treated for further processing of unidirectional prepreg tapes. Continuous lengths of Dodecamethylenediamine treated CN80 pitch fiber being spooled onto a three inch core can be seen in Figure 7.
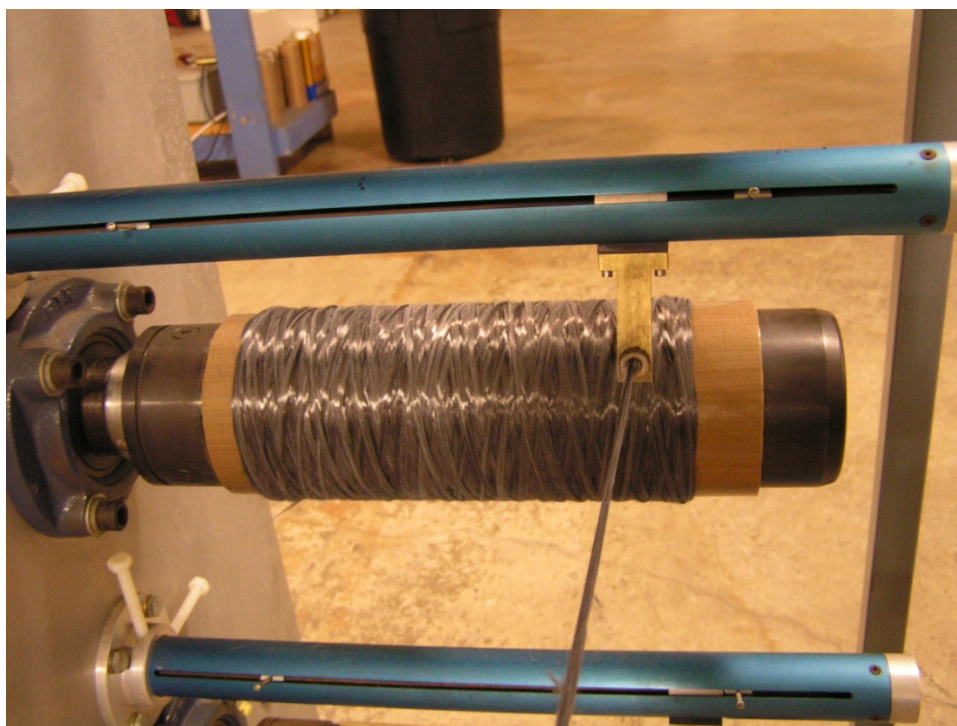
**Figure 7. Spooling Dodecamethylenediamine Treated Pitch Fiber**

### 4.1.3 X-Ray Photoelectron Spectroscopy

The XPS results have confirmed pitch fiber functionalization with distinct alterations in chemical composition of the fiber surface. By further analyzing the binding energies of the XPS results, the relative molecular structure of the fiber surface can be determined. Based on the peak distribution, two overlapping curves can be distinguished for both the C1s and O1s peaks. Table 3 and Table 4 indicate the binding energy for each overlapping peak, the type of bond associated with each bonding energy, and the relative concentration of each peak for C1s and O1s curves, respectively. Example C1s and O1s XPS curve breakdowns are shown for the maleic anhydride treated fiber in Figure 8 and Figure 9, respectively.

**Table 3. Peak Breakdown of $C_{1s}$ XPS Curves**

|  | Binding Energy (eV) | % | Bond Type | Binding Energy (eV) | % | Bond Type |
|---|---|---|---|---|---|---|
| Desized | 284.87 | 73.54 | Hydrocarbon | 286.49 | 26.20 | Ether |
| Maleic | 284.84 | 89.98 | Hydrocarbon | 286.34 | 4.69 | Ether |
| Dodeca | 284.68 | 94.52 | Hydrocarbon | 286.18 | 5.01 | Ether |
| p-PDA | 284.86 | 90.11 | Hydrocarbon | 286.36 | 6.58 | Ether |
| Hexa | 284.86 | 91.72 | Hydrocarbon | 286.36 | 7.16 | Ether |
| Bis-M | 284.86 | 84.45 | Hydrocarbon | 286.36 | 13.09 | Ether |

**Table 4. Peak Breakdown of O$_{1s}$ XPS Curves**

|  | Binding Energy (eV) | % | Bond Type | Binding Energy (eV) | % | Bond Type |
|---|---|---|---|---|---|---|
| Desized | 532.67 | 46.00 | Carbonyl | 533.52 | 54.00 | Ester |
| Maleic | 532.08 | 32.79 | Carbonyl | 533.34 | 67.21 | Ester |
| Dodeca | 531.18 | 61.53 | Carbonyl | 532.70 | 38.47 | Ester |
| p-PDA | 532.15 | 49.68 | Carbonyl | 533.41 | 50.32 | Ester |
| Hexa | 532.11 | 46.87 | Carbonyl | 533.49 | 53.13 | Ester |
| Bis-M | 532.03 | 46.64 | Carbonyl | 533.43 | 53.36 | Ester |
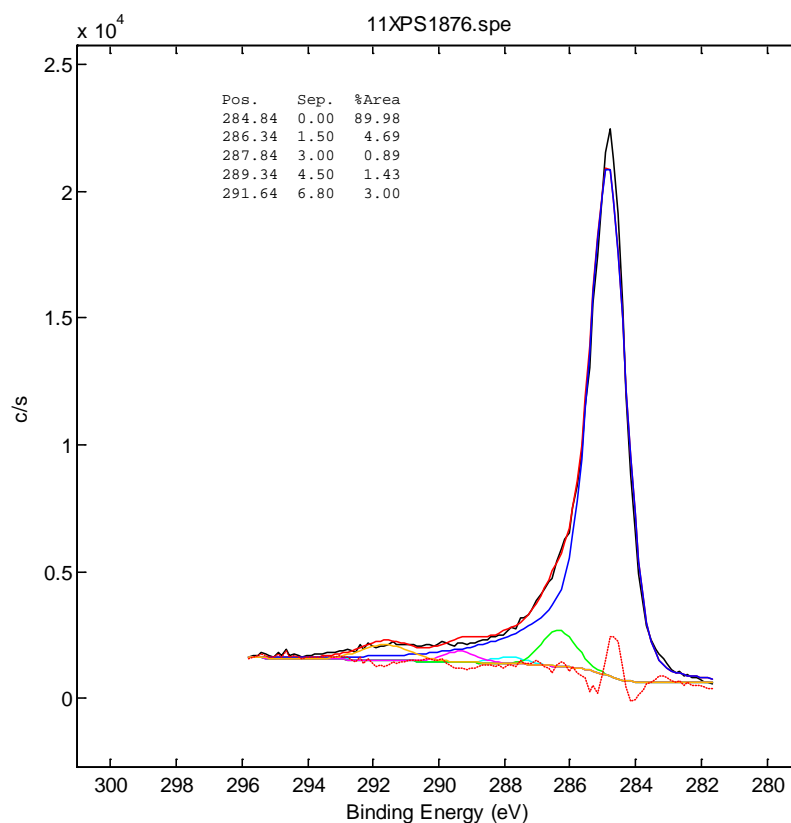


**Figure 8. C1s XPS Peak for Maleic Anhydride Treated CN80 Pitch Carbon Fiber**

11XPS1876.spe

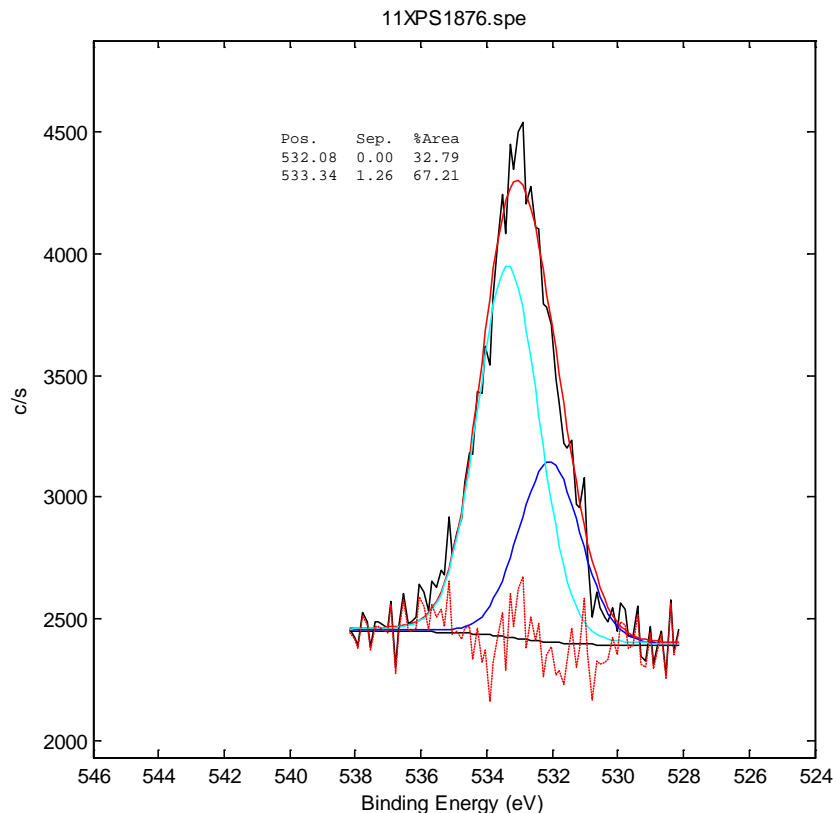| Pos. | Sep. | %Area |
|---|---|---|
| 532.08 | 0.00 | 32.79 |
| 533.34 | 1.26 | 67.21 |

**Figure 9. O1s XPS Peak for Maleic Anhydride Treated CN80 Pitch Carbon Fiber**

Further analysis of the XPS results from diamine functionalization without prior maleic anhydride surface treatment shows a significant inconsistency with little to no conclusive treatment chemistry. The analysis, provided by MSU, indicated an array of carbon bonding from as little as 27% to as much as 91% aliphatic carbon bonding, as well as carbon bonded to a single oxygen from as little as 2.49% to as much as 52.2% for the various functionalizations. The disparity in results was due to inconsistencies in the fiber desizing and subsequent surface treatment.

**4.2 Pitch Fiber Nanofin Modifications**

**4.2.1 Michigan State University Nanofin Modification Work**

**4.2.1.1 Plasma Treatment of Fibers**

The single fiber tensile testing performed on the thermally desized CN80 gave a value of 369 ± 76 ksi (n = 17). The surface of the untreated Granoc CN80 fiber was found to have some features that appeared to be debris or residue, Figure 10.
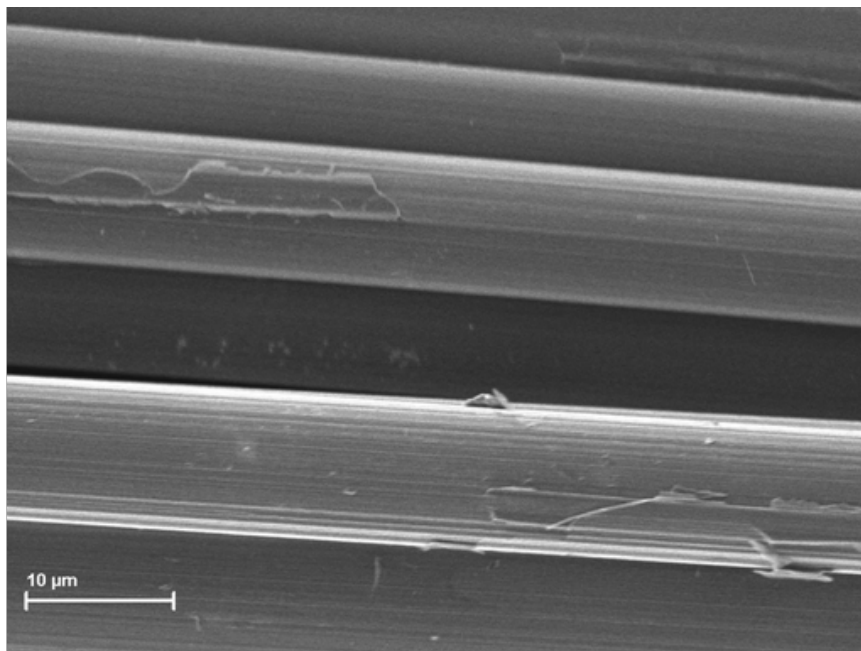
**Figure 10. Granoc CN80 Thermally Desized Control**

A higher magnification view of the CN80 control is shown in Figure 11. The surface of the plasma treated CN80 fibers, Figure 12, appeared free of debris with no evidence of extensive pedal-like growth.
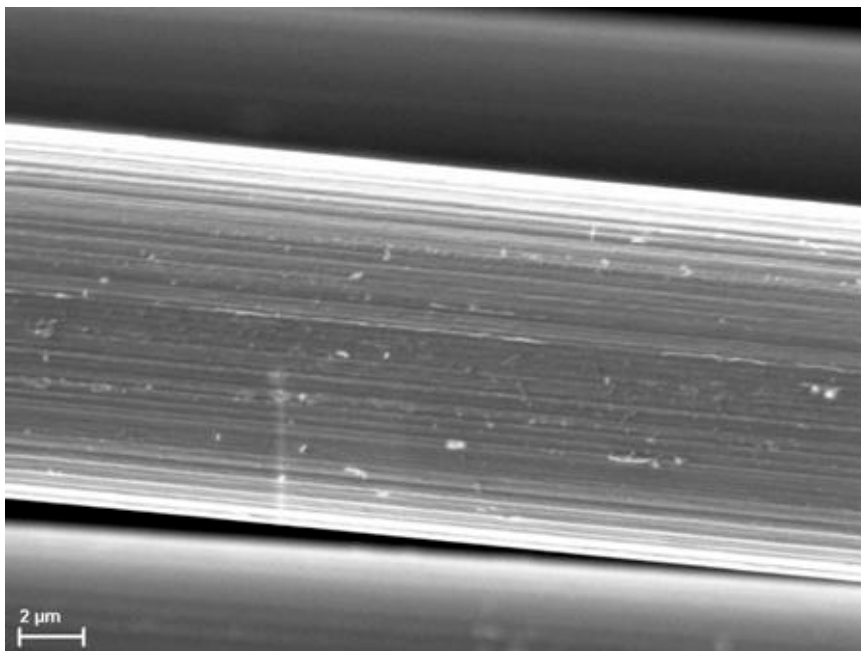


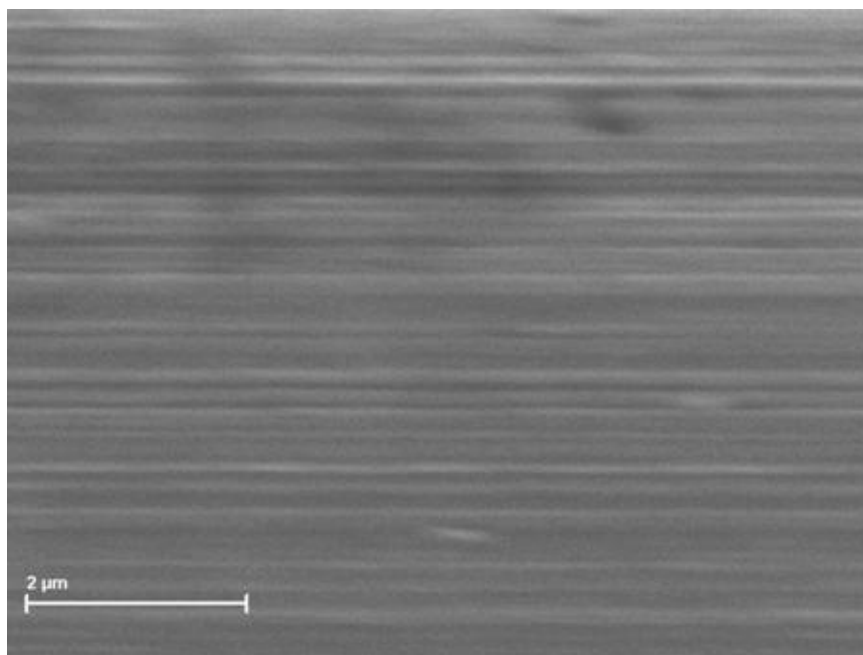**Figure 11. Granoc CN80 Thermally Desized Control**

**Figure 12. Granoc CN80 Plasma Treated, 75% Power**

The surfaces of the plasma treated AS4 fibers, Figure 13, and Dialead K63712 fibers, Figure 14, did not show evidence of nanofin growth. The feature shown at the top center of Figure 4 was not seen on other sections of the fiber.
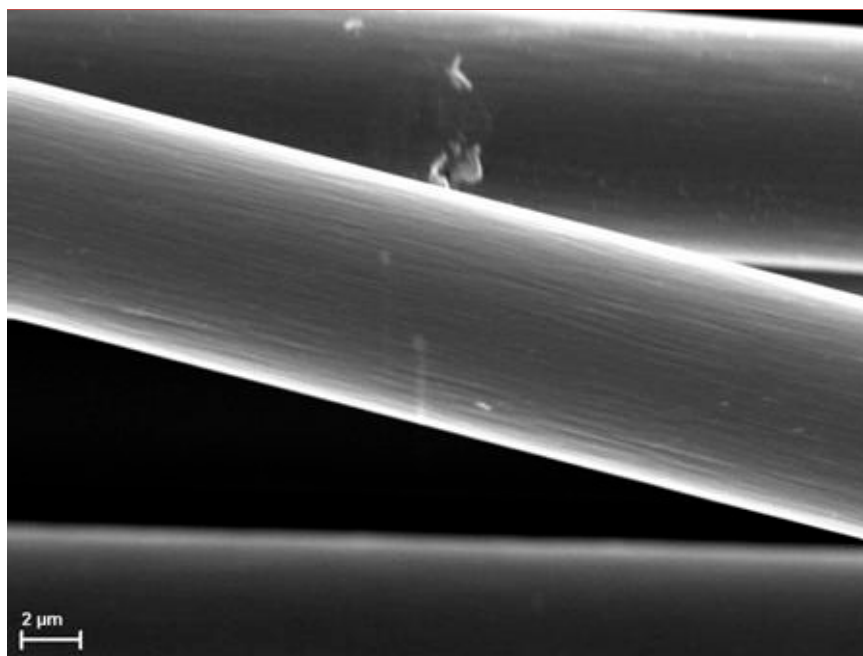


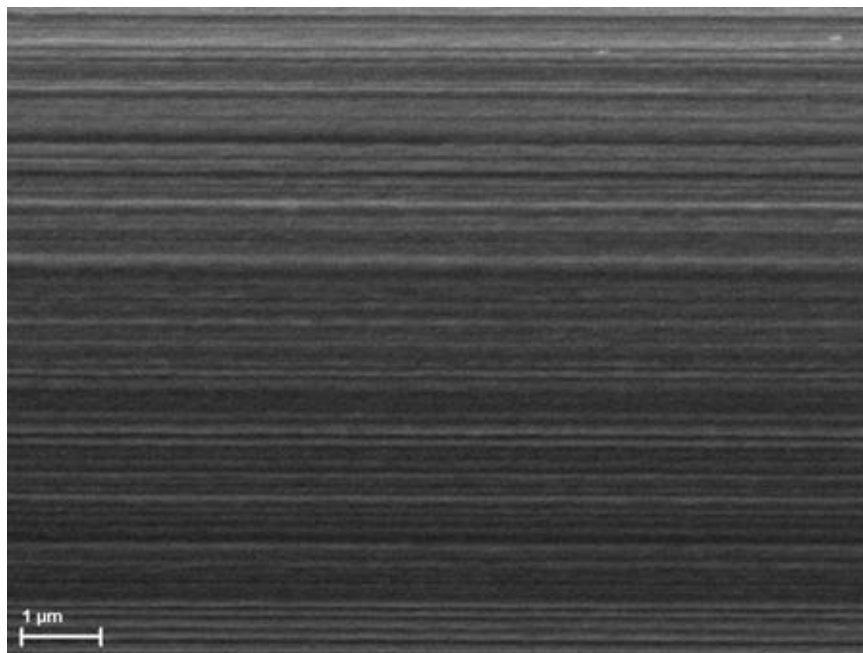**Figure 13. AS4-12k Plasma Treated, 75% Power**

**Figure 14. Dialead K63712 Plasma Treated, 75% Power**

Lastly, the resulting effect of the 1% power experiment is shown in Figure 15. The surface of the Dialead K63712 fiber exhibited no change in structure. Therefore, attempts at using RF plasma to grow nanofin structures on pitch or PAN based carbon fibers were unsuccessful.
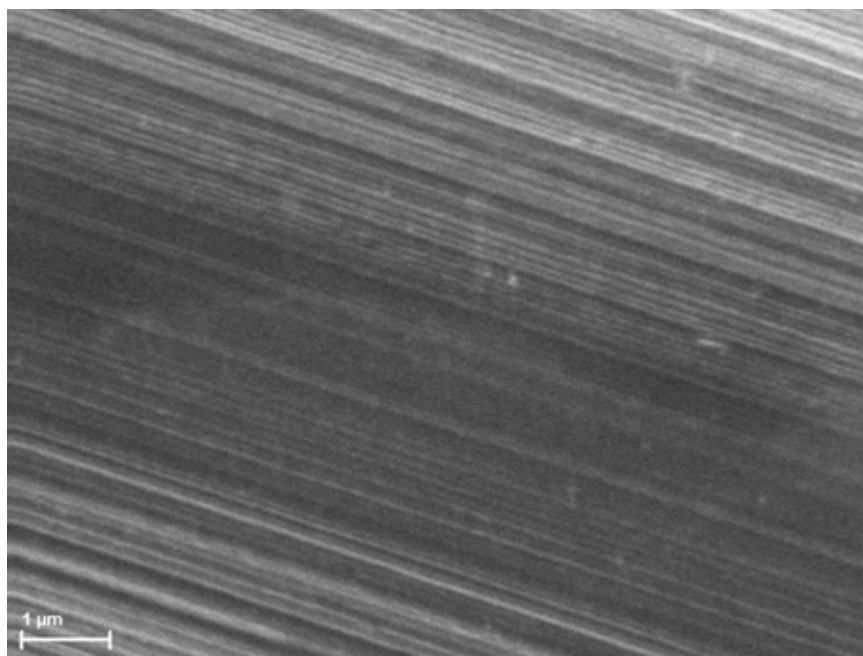


**Figure 15. Dialead K63712 - Plasma Treated, 1% Power**

### 4.2.1.2 Previous Carbon Fiber Treatment Work

Renewed collaborations with the plasma team at MSU to participate in this program were extended, and well received by MSUs colleagues. However, the plasma team had other higher priority contractual work that interfered with scheduling of the plasma work. Secondly, personnel compliant with the EAR restrictions of this contract were creating difficulties in identifying the technical staff to do the treatments. Because of these restrictions, microwave plasma treatments were not able to be conducted at MSU before the program end date. If there were more resources with respect to time and funds, a team at MSU would be assembled to further explore the feasibility of growing carbon nanostructures on fibers to enhance the thermal conductivity of organic matrix composites.

### 4.3 Silver Polyimide Formulation

The initial formulation of silverized polyimide proved successful. The silver(I) acetate gelled with the poly(amic acid), as expected, to form a homogenous doped resin complex. A small amount of the doped resin is shown in Figure 16, illustrating proper translucency. Also in Figure 16, the thermally cured 2 inch by 2 inch, silverized laminae is shown next to a control piece of the T650-35 fabric for comparison. The figure clearly illustrates a uniform, reflective silver surface following thermal treatment of the metalized resin.
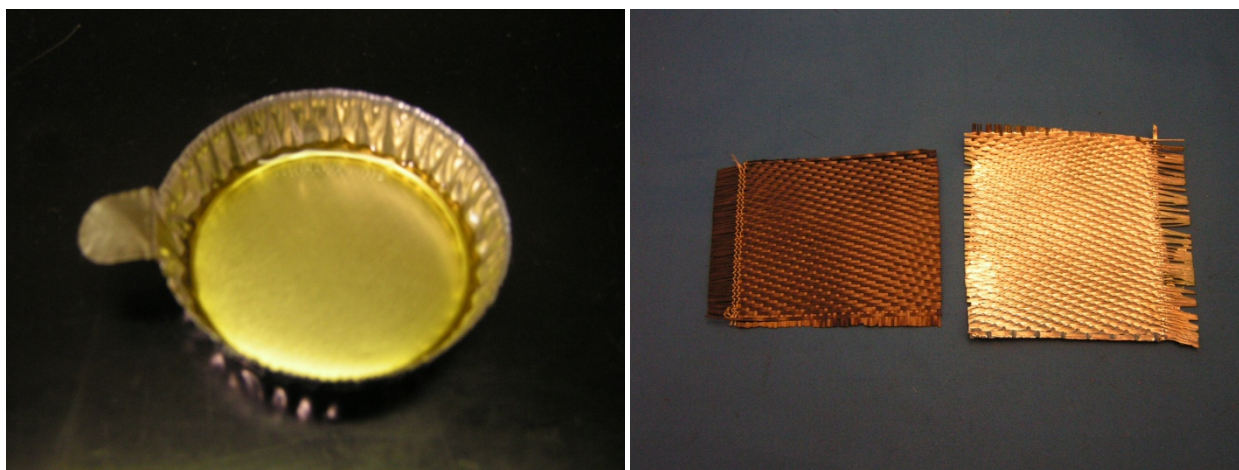


**Figure 16. Left: Sample of Uncured Doped Resin; Right: Laminae Following Thermal Cure Beside Control Fabric**

### 4.4 Pitch Fiber Composite Fabrication

### 4.4.1 Epoxy Matrix Composites

### 4.4.1.1 Three-Dimensional Pitch Epoxy Composites

Three pitch fiber composite panels were fabricated using the three-dimensional preforms with 5, 6, and 8 ppi loading densities. Figure 17 shows a dry pitch fiber preform and a fabricated three-

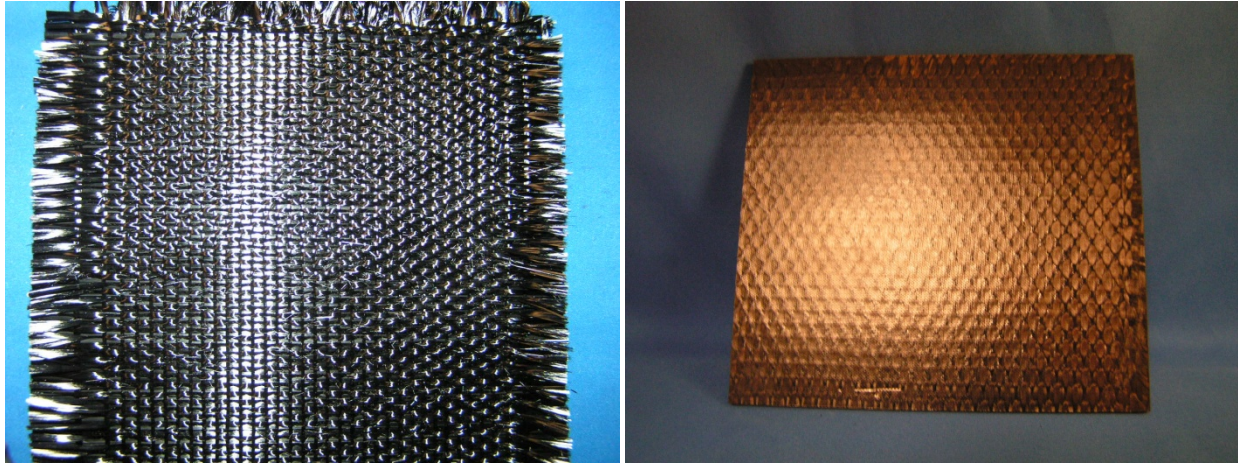dimensional pitch fiber composite, respectively.  The edges of the panels were discarded due to fiber washing.



**Figure 17. Three-Dimensional Pitch Fiber Preform and Fabricated Three-Dimensional Composite, Respectively**

The first panel of 5 ppi loading density was properly compressed with a thickness of 2.18 mm. Acid digestion analysis indicated a fiber volume fraction of 48.35% and a panel density of 1.70 g/cm$^3$.  The panel was machined for microscopy, thermal conductivity, short beam shear and flexure testing.  Warp and fill direction microscopy are shown in Figure 18.  The images show quality compaction with minimal porosity. Additionally, the fiber orientation is clearly illustrated.  Thermal conductivity testing of the pitch fiber composite indicated a transverse (through-thickness) thermal conductivity of 4.27 W/mK, 58% higher than typical laminated pitch fiber epoxy composites.  The flexure strength was measured in the warp direction at approximately 472 MPa, with a standard deviation of 12.7, and in the fill direction at approximately 247.2 MPa, with a standard deviation of 22.6.  The warp flexure strength results are approximately 19% lower than standard unidirectional pitch fiber/epoxy composites, likely due to the lower fiber loading in the warp direction with an additional fiber crimping effect. Short beam shear strength was measured in the warp direction at approximately 40.3 MPa with a standard deviation of 2.0, and in the fill direction at approximately 19.2 MPa with a standard deviation of 2.0.  The measured warp direction short beam shear strength is 33% lower than the standard unidirectional composites, again due to the reduced fiber loading.
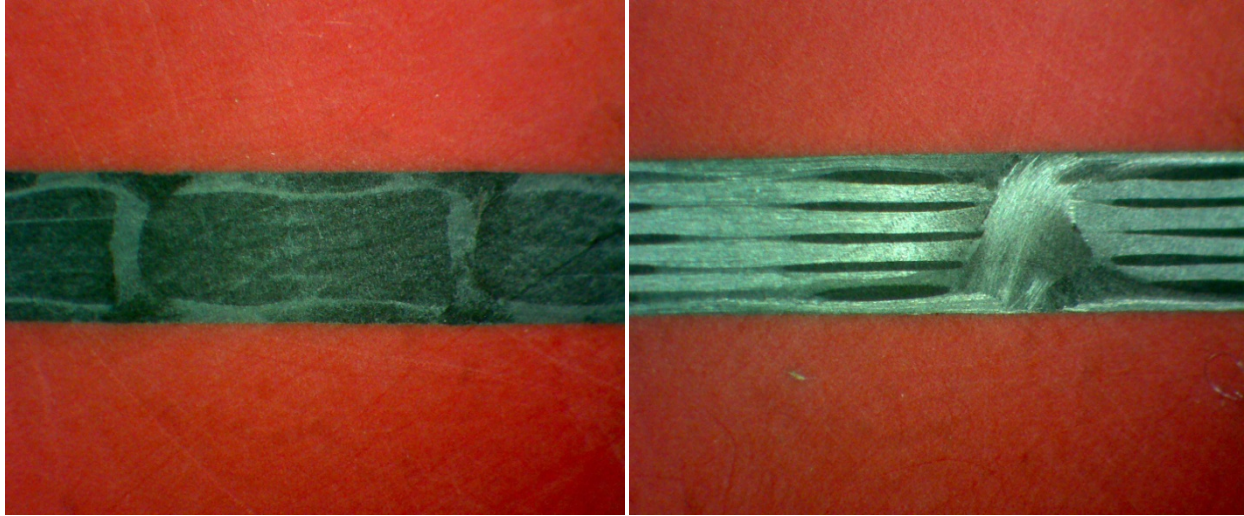
**Figure 18. Cross Sectional Images of Panel 1 in Warp and Fill Directions, Respectively**

The second pitch fiber panel was of 8 ppi loading density; however, insufficient resin flashing and part compaction occurred, causing the resultant composite panel to be resin rich and 3 mm too thick. Therefore, only microscopy and thermal conductivity was performed on the second panel. The microscopy images in both the warp and fill directions are shown in Figure 19. The preform construction is clearly illustrated. However, improper compaction is evidenced by the excess epoxy throughout. For thermal conductivity testing, the excess epoxy was machined down to expose the underlying fibers. The thermal conductivity through the thickness of the panel was measured at 3.58 W/mK. The acid digestion analysis also indicated improper compaction with a fiber volume fraction of 18.79%; however, it should be noted that some fiber was trapped in the washing filter, due to splintering of the pitch fiber reinforcement. Therefore, the fiber volume fraction is likely higher than the indicated 18.79%, but not significantly higher. The density of the panel was also measured at 1.40 g/cm$^3$.
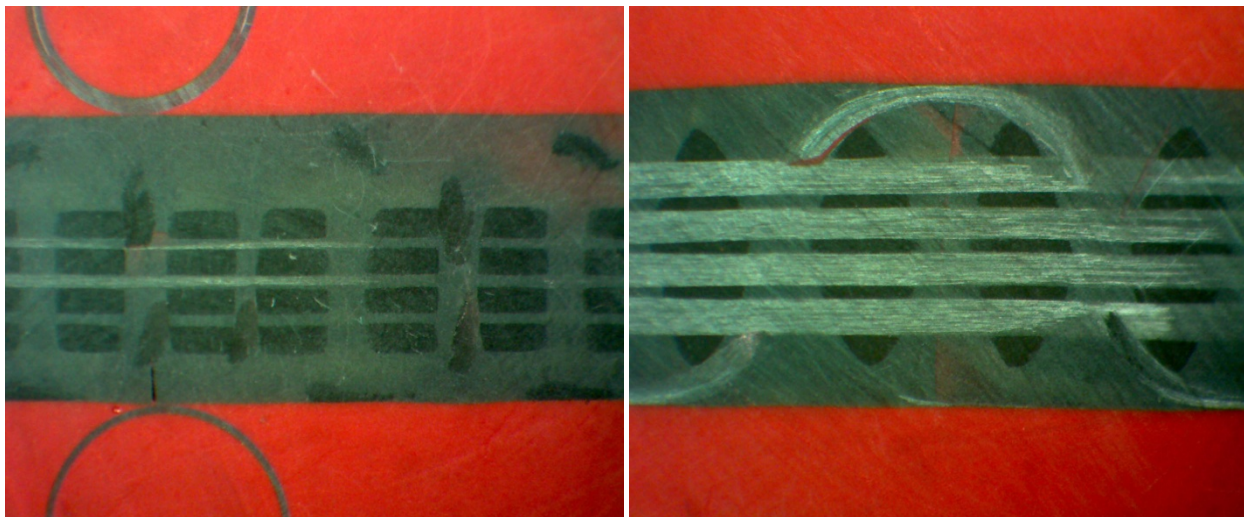


**Figure 19. Cross Sectional Images of Panel 2 in Warp and Fill Directions, Respectively**

The third panel was of 6 ppi loading density. The part was properly compressed with a thickness of 3.70 mm. Acid digestion analysis suggested a fiber volume fraction of 26.37% with a panel density of 1.49 g/cm$^3$. The panel was machined for microscopy, thermal conductivity, and flexure testing. The microscopy images of the warp and fill directions are shown in Figure 20. The images show proper compaction with minimal porosity. Thermal conductivity testing of the pitch fiber composite indicated a transverse (through thickness) thermal conductivity of 2.52 W/mK. Flexure testing resulted in a warp direction flexure strength of 322.7 MPa, with a standard deviation of 22.7, and a fill direction flexure strength of 258.7 MPa, with a standard deviation of 33.7. Short beam shear strength was measured in the warp direction at approximately 43.1 MPa with a standard deviation of 1.0, and in the fill direction at approximately 23.0 MPa with a standard deviation of 1.2.
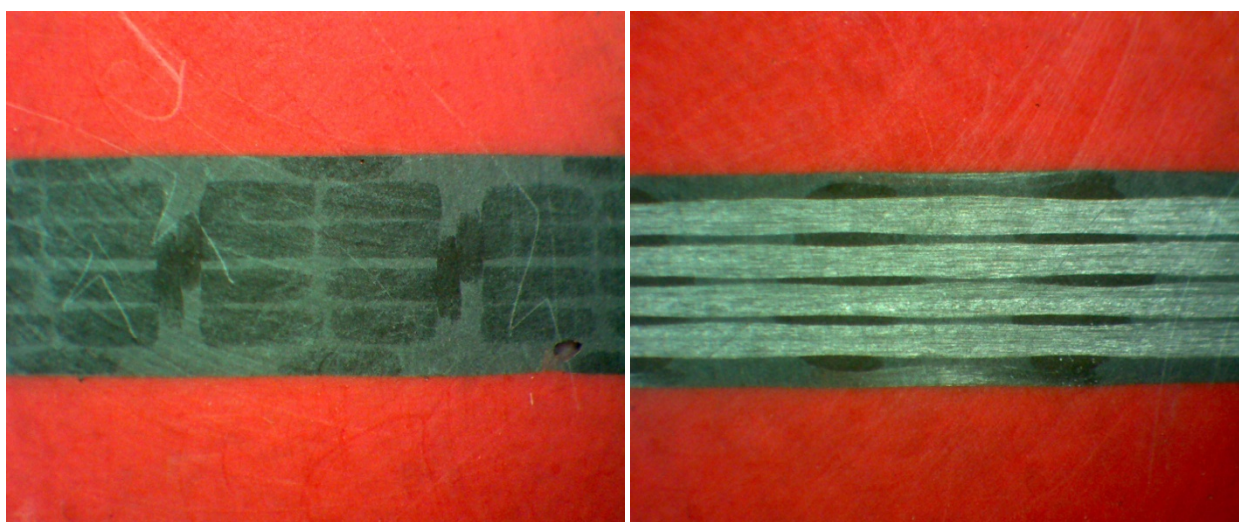


**Figure 20. Cross Sectional Images of Panel 3 in Warp and Fill Directions, Respectively**

### 4.4.1.2 Amine Functionalized Pitch Epoxy Composites

The mechanical and thermal properties of the unidirectional, amine functionalized (p-PDA and dodecamethylenediamine) pitch fiber composites were compared to a control CN80 pitch panel to analyze the effectiveness of the amine functionalization. The mechanical properties of interest here were short beam shear strength (ASTM D2344) and double-notch shear strength (ASTM D3846). The testing results are shown in Table 5. The displayed results clearly illustrate a tremendous enhancement in both short beam shear and double-notch shear strength for the p-PDA and dodecamethylenediamine treated composites, as compared to CN80 control. The significant enhancement in shear properties is a direct result of the augmented mechanical attachment between the fiber and the matrix materials that the diamine functionalization provides. It should also be noted that the diamine treated double-notch shear samples predominately failed due to buckling, not shear failure, indicating the actual shear strength may be to some extent higher than the reported value.

**Table 5. Unidirectional Pitch Epoxy Composite Results**

| Composite Type | SBS Strength | DNS Strength | Transverse Thermal Conductivity | Axial Thermal Conductivity |
|---|---|---|---|---|
| | (MPa) | (MPa) | (W/mK) | (W/mK) |
| CN80 Control | 20.54 ± 3.22 | 11.33 ± 1.30 | 1.791 | 118.63 |
| p-PDA Treated | 59.14 ± 6.13 | 32.41 ± 1.10 | 1.25 | 191.52 |
| 1,12-Diamine Treated | 56.49 ± 0.804 | 32.063 ± 2.814 | 2.235 | 161.14 |

The in-plane and out-of-plane thermal conductivities were also compared and are shown in Table 5. The transverse thermal conductivity, which is of focus here, was enhanced by nearly 25% with dodecamethylenediamine functionalization. This increase in through-thickness thermal conductivity is a direct result of the covalent bonding between the fiber and matrix materials. The covalent bonds provide a direct pathway for thermal transport through the composite. The p-PDA treatment indicated a slight decrease in transverse thermal conductivity, which may be a result of the inaccuracies of the testing methods. The axial thermal conductivity was also improved significantly for both diamine functionalizations.

### 4.4.1.3 Nickel Coated PAN Epoxy Composites

The nickel coated PAN carbon fiber epoxy composite was investigated to determine the applicability of a metalized coating on the surface of the fiber for improved thermal conductivity. The nickel coated PAN fiber was in stock at P$^2$SI. The supplier of the fiber indicated that nickel coating pitch carbon fiber may be possible, but could be problematic due to the general frailty of the fiber. The transverse thermal conductivity of the composite measured 0.7935 W/mK and the in-plane thermal conductivity measured 8.557 W/mK. These values are not significantly higher than standard PAN reinforced epoxy composites; therefore the nickel based coating was not explored further. The double-notch shear strength measure 44.378 MPa with a standard deviation of 14.505. The short beam shear strength measure 69.50 MPa with a standard deviation of 0.983.

### 4.4.2 Polyimide Matrix Composites

### 4.4.2.1 Unidirectional Pitch Polyimide Composites

The dodecamethylenediamine surface treatment was also evaluated for polyimide matrix composites. The 12-ply, functionalized polyimide composite was compared to a unidirectional, desized CN80 12-ply laminate. The panels were evaluated for short beam shear, double-notch shear, and in-plane and out-of-plane thermal conductivity. The results are shown in Table 6. The results indicate an over 33% increase in short beam shear strength and a nearly 30% increase in transverse thermal conductivity for the diamine treated composite over the pitch fiber control. However, a slight decrease in double-notch shear strength was observed, likely due to porosity in the initial panels.

**Table 6. Unidirectional Polyimide Pitch Composite Results**

| Composite Type | SBS Strength | DNS Strength | Transverse Thermal Conductivity | Axial Thermal Conductivity |
|---|---|---|---|---|
| | (MPa) | (MPa) | (W/mK) | (W/mK) |
| CN80 Control | 24.85 ± 0.739 | 14.37 ± 2.973 | 0.6288 | 131.692 |
| 1,12-Diamine Treated | 33.22 ± 1.404 | 11.35 ± 2.361 | 0.8136 | 191.18 |

### 4.4.2.2 Three-Dimensional Pitch Polyimide Composites

The control and diamine treated 3D pitch polyimide composites are shown in Figure 21, respectively. Due to excess handling (desizing, ozone treatment, and diamine treatment) of the diamine treated preform, considerable washing of the fibers was apparent, as shown in the figure. The fiber washing can have a considerable effect on material properties.
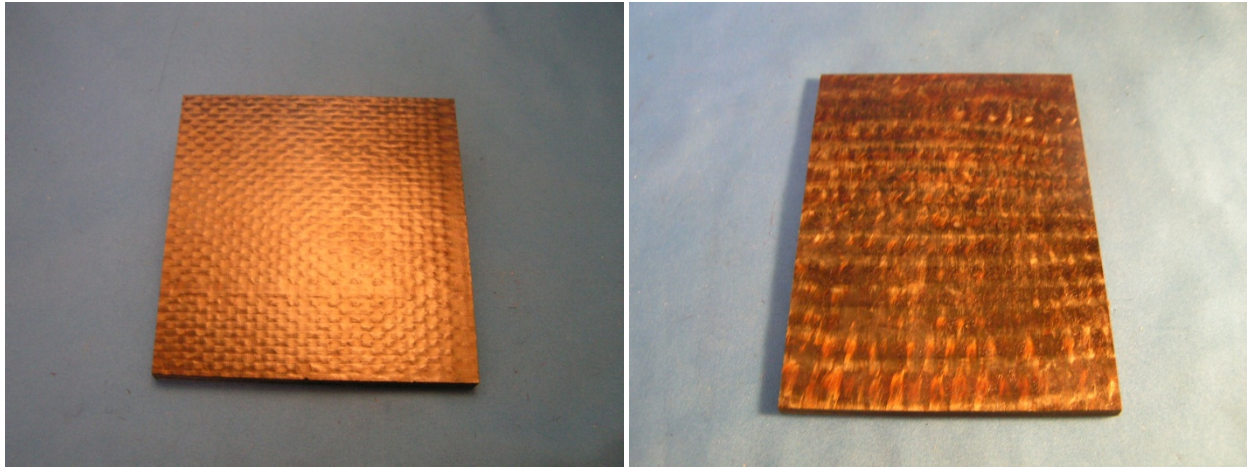


**Figure 21. Three-Dimensional Pitch Polyimide Composites**

The three-dimensional pitch polyimide composites were mechanically tested by three-point flexure testing and thermally tested by the through-thickness guarded-hot-plate technique. The control flexure strengths in the warp and fill fiber directions were 174.97 MPa and 272.10 MPa with standard deviations of 4.46 and 27.51 respectively. The diamine treated flexure strengths in the warp and fill directions were 156.39 MPa and 298.20 MPa with standard deviations of 11.07 and 58.76 respectively. Therefore, no considerable variance in mechanical properties was observed. There was, however, a significant difference in thermal conductivity. The control panel thermal conductivity was measured 4.524 W/mK, while the diamine treated thermal conductivity was measured 0.580 W/mK. The drastic drop in thermal conductivity is believed to be a result of high levels of porosity within the diamine treated composite, as can be seen in Figure 22.
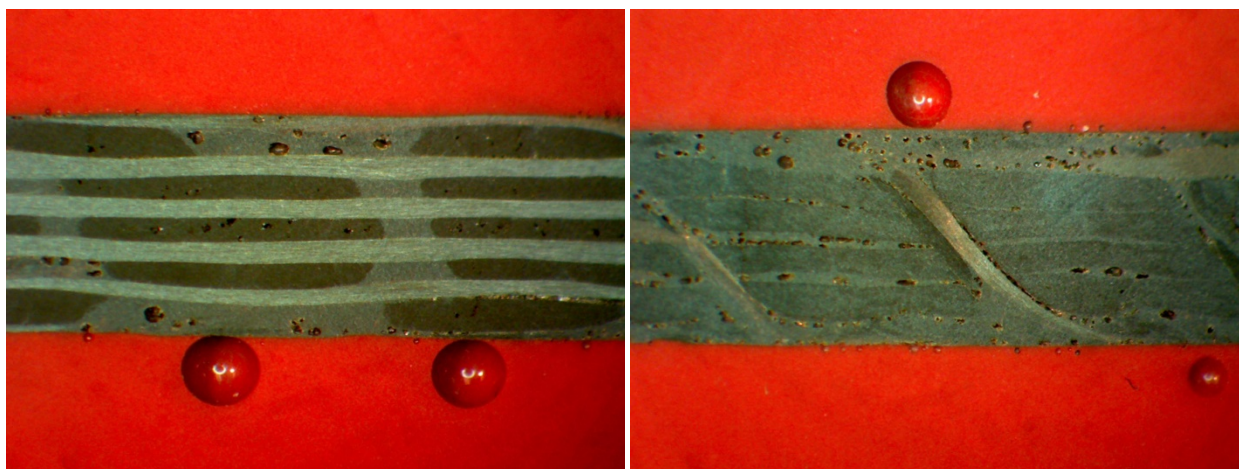
**Figure 22. Diamine Treated Three-Dimensional Pitch Polyimide Composite Micrographs**

An additional diamine treated 3D composite was fabricated for reevaluation. Unfortunately, the preform weave used previously was depleted, forcing use of an alternate preform with a dissimilar weaving density. The part was fabricated as before and machined for through thickness thermal conductivity measurement and short beam shear strength evaluations in both the warp and fill directions. The warp and fill directional shear strengths were very similar with an average warp shear strength of 16.71 MPa and average fill shear strength of 16.46 MPa, and respective standard deviations of 6.12 and 3.40 MPa. The resultant through-thickness thermal conductivity was measured at 0.542 W/mK, significantly lower than expected. The low thermal conductivity is believed to be due to the alternate preform construction. In addition, with such a low through thickness thermal conductivity, one has to question the preform construction and whether the z-direction yarn was a pitch based fiber.

### 4.4.2.3 Silver Polyimide Composites

The initial, one ply silver polyimide laminae was evaluated for through thickness thermal conductivity using the guarded-hot-plate technique. The resultant value was measured as 0.189 W/mK. It should be noted, however, that the technique is not intended for use with very thin samples. In addition, the sample was not machined flat and parallel, as the standard calls for. Therefore, the measured value should not be taken quantitatively.

The compression cured, 4-ply silver polyimide laminate is shown in Figure 23. It is clear from the images that the compression cured laminate did not exhibit the uniform, classic silver color across the surface of the fabric, as the one-ply laminae did. Instead, the surface of the composite appears non-uniform with a dull, tarnished silver surface. This is likely due to the variance in processing and conditions. The silver polyimide laminate was machined and tested for through-thickness thermal conductivity. The guarded-hot-plate technique yielded a thermal conductivity value of 0.64 W/mK, which compares to the unidirectional control composite, made with the same CN80-30s pitch fiber, with a thermal conductivity of 0.65 W/mK. Therefore, the metalized polyimide does not appear to provide any considerable enhancement to the thermal properties of the composite.
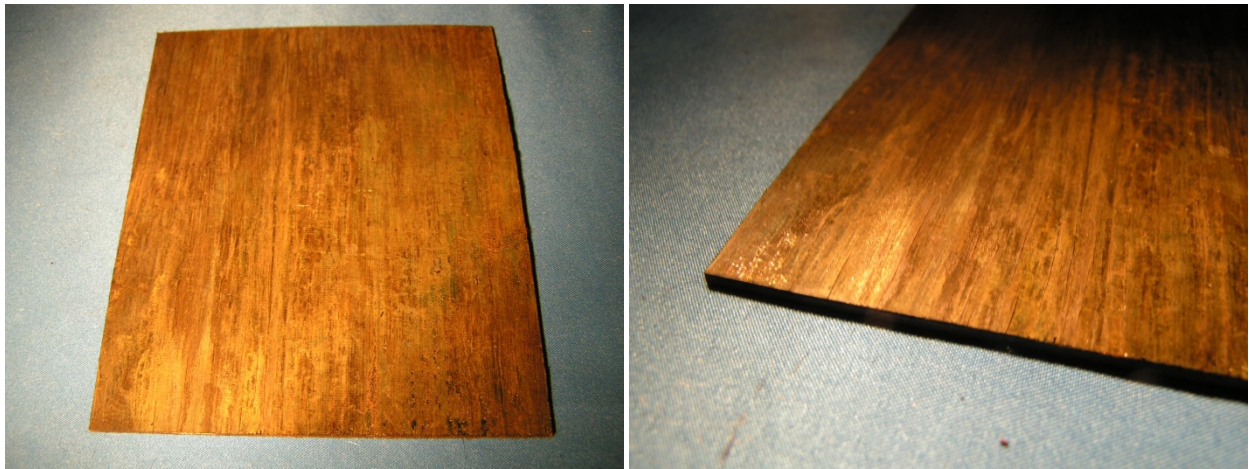
**Figure 23. 4-Ply Silver Polyimide Laminate**

# 5. CONCLUSIONS

Through the STTR program for the development of thermally conductive structural two-dimensional composite materials, successful fiber functionalization was realized through maleic anhydride and various diamine fiber treatments. XPS results of the treated fibers indicated a significant chemical alteration for both the maleic anhydride and diamine functionalizations. The chemical alterations provide hosts for covalent bonding between the fiber surface and matrix material, leading to significant improvements (over 30%) in both mechanical and thermal properties of the composite.

Additional modifications were attempted with limited success. The growth of graphene nanofins on the surface of the pitch carbon fibers was pursued, using a RFPE-CVD technique, but proved unsuccessful. Other forms of modifications included metalizing the fiber surface using a nickel coating and metalizing the polyimide resin matrix. The benefits of these methods were not apparent.

To date, three-dimensional non-crimp fabrics engineered for maximum through-thickness thermal conductivity, combined with our novel fiber surface treatments and a polyimide matrix appear to offer the highest pay-off pitch fiber composites in terms of optimizing thermal and mechanical properties.

# 6. REFERENCES

1. Bhuvana, T., Kumar, A., Sood, A., Gerzeski, R., Hu, J., Bhadram, V., Narayana, C., Fisher, S., "Contiguous Petal-Like Carbon Nanosheet Outgrowths from Graphite Fibers by Plasma CVD," *Appld Mater Interf* In Press (2009)
2. Curliss, D., Lincoln, J., "Vapor Grown Carbon Fiber Reinforced Composite Materials and Methods of Making and Using Same," *US Patent 7,338,684* (2008)
3. Askeland, P., Rich M., Drzal, L., "The Effect of Photo-oxidation Surface Treatment for Adhesion Promotion in Carbon Fiber-Epoxy Composites," *Proc Adhesion Soc Ann Conf* (2004)
4. Drzal, L., Rich, M., "Process for the Treatment of a Fiber," *US Patent 6,648,973* (2003)
5. Drzal, L., Rich, M., "Process for the Treatment of a Fiber," *US Patent 6,649,225* (2003)
6. Curliss, D., Lincoln, J., "Innovative Fiber Treatment and Sizing Technology for High Performance Vinyl Ester Matrix Composite Materials," *Navy Contract N65538-04-M-0141* (2004)
7. Curliss, D., "Innovative Approach for High Strength, High Thermal Conductivity Composite Materials," *Air Force Contract FA8650-10-M-5105* (2010)
8. Suzuki, Omehara *Carbon* **37** 47 (1999)
9. Wang, J., Zhu, M., Outlaw, R., Zhao, X., Manos, D., Holloway, B., "Synthesis of Carbon Nanosheets by Inductively Coupled Radio-Frequency Plasma Enhanced Chemical Vapor Deposition," *Carbon* **42** 2867 (2004)
10. Clancy, T., Frankland, S., Hinkley, J., Gates, T., "Multiscale Modeling of Thermal Conductivity of Polymer/Carbon Nanocomposites," *Int J Thermal Sci* **49** 1555 (2010)
11. Clancy, T., Gates, T., "Modeling of Interfacial Modification Effects on Thermal Conductivity of Carbon Nanotube Composites," *Polymer* **47** 5990 (2006)
12. Thompson, D Scott, *et al*. "Single –Stage Synthesis and Characterization of Relective and Conductive Silver – Polyimide Films Prepared from Silver(I) Complexes with ODPA/4,4'-ODA," *ACS Applied Materials & Interfaces* **1** 1457 (2009).
13. Southward, Robin E., Thompson David W. "Reflective and Conductive Silvered Polyimide Films for Space Applications Prepared via a Novel Single-Stage Self-Metallization Technique," *Mater Design* **22** 565 (2001).
14. Southward, Robin E., Stoakley, Diane M. "Reflective and Electrically Conductive Surface Silvered Polyimide Films and Coatings Prepared via Unusual Single-Stage Self-Metallization Techniques," *Prog Org Coat* **41** 99 (2001).